

Preprint Submitted to the American Chemical Society
Fuels Division, National Meeting, New York City Aug. 1991

CYCLOPENTADIENE AND CYCLOPENTADIENYL CONVERSION DURING
BENZENE OXIDATION, THERMODYNAMIC AND MECHANISTIC CONSIDERATIONS.

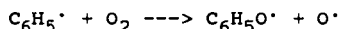
Joseph W Bozzelli, Viral Desai, Edward R Ritter and Anthony M. Dean*
Dept of Chemical Engineering and Chemistry,
New Jersey Inst. of Technology, Newark, NJ 07039,
*Exxon Research And Engineering, Annandale, NJ 08801

Abstract

There are a number of studies on benzene oxidation and pyrolysis, yet we do not know of a detailed reaction mechanism based on fundamental kinetic and thermodynamic principles that explains published experimental observations. Benzene reacts by H transfer (abstraction) forming phenyl radicals. Prior to unimolecular decomposition, phenyl can react with O_2 , O or HO_2 to form a phenoxy radical. Phenoxy, the major channel for benzene loss, has been shown to decompose to CO plus cyclopentadienyl radical. In this study, we focus on the oxidation pathways to loss of cyclopentadienyl species. We specifically consider thermodynamic and kinetic analyses for reactions of cyclopentadiene and cyclopentadienyl radical with O_2 , O, H, OH and HO_2 . Rate constants as functions of pressure and temperature for the radical addition and recombination reactions are calculated using bimolecular QRRK theory. We compare predictions from our mechanism with phenoxy and benzene reaction data.

INTRODUCTION

Benzene reacts in the presence of oxygen (through phenyl or cyclohexadienyl radical intermediates) to form phenyl and phenoxy radicals in addition to stable phenol molecules. Phenyl radicals in the presence of oxygen will undergo the rapid, exothermic, chain branching reaction:



The phenoxy and cyclohexadienyl radical intermediates are resonantly stabilized and are usually present at higher concentrations than the more reactive phenyl or other non-stabilized radicals. The phenoxy radical has been shown to unimolecularly react to produce carbon monoxide and cyclopentadienyl (CyCpdj) radical^{1,2}, while cyclohexadienyl radical produces methyl and CyCpdj³. Cyclopentadienyl radical is highly resonantly stabilized with references on its heat of formation ranging in value from 57 to 45 Kcal/mole corresponding to a resonance stabilization energy (RSE)^{4,5} of ca. 18 to 30 Kcal/mole. This large RSE essentially eliminates reaction of this radical with O_2 to form a peroxy radical, which is favorable for normal alkyl radicals. This occurs due to the very low, ca 11 Kcal/mole, well depth for

stabilizing the adduct with significant loss of entropy.

Our initial attempts to construct a mechanism comprised of elementary reactions to model benzene production and loss, for comparisons to our experiments on chlorobenzene and dichlorobenzene pyrolysis reaction in H_2 ,^{3,6} chlorobenzene oxidation⁶ or the benzene oxidation data of Brezinsky⁷, have produced relatively large concentrations of cyclopentadienyl radical (Cycpdj). Calculations, incorporating abstraction reactions for this radical, indicate it would build up to concentrations equal to or larger than its cyclopentadiene parent and would clearly act as a bottle-neck to benzene loss. The reactions in our mechanisms included microscopic-reversibility and showed that the benzene, phenyl, cyclohexadienyl - phenoxy system would essentially remain at steady state.

Phenols and phenoxy species are known to be common intermediates in oxidation of aromatic species and they are considered strong candidates as precursors in formation of dibenzofurans and dioxins. Knowledge of important reactions of phenoxy decomposition products - Cycpdj and its parent is therefore critical to understanding possible formation of dibenzofurans and dioxins, through reverse reactions, as well as their destruction.

Aromatic species are also important in motor fuels, with small ring aromatics often used to increase octane rating in gasolines,⁷ since lead has been eliminated as a blending ingredient. Understanding the fundamental reactions of these aromatic species will clearly benefit researchers who are working to understand preignition and engine knock. This understanding may also have implications for soot formation in diesels.

In formulating a detailed model of benzene destruction and/or formation in varied oxidation or pyrolysis environments, we need to consider the decomposition pathways for these resonantly stabilized cyclopentadienyl and phenoxy species. We currently do not know of any reaction mechanism for benzene oxidation comprised of elementary reactions, which are based upon fundamental thermochemical kinetic principles. Brezinsky⁷ and Venkat et. al.⁸ have published general reaction schemes, with no rate constants or thermodynamic properties. Bittker⁹ published a mechanism which was based upon previously published reaction paths and presented rate constants which fit experimental data for ignition delay times and toluene loss profiles. Bittker, however, used a sensitivity code to determine the important reactions and then optimized the fit of the data by adjusting rate constants. No account for collisional fall-off of activated complexes formed by addition of atoms or radicals to unsaturated (olefinic or aromatic) bonds, or by combination of radical species was included. Published mechanisms for toluene and other aromatic pyrolysis sometimes include reactions where the Arrhenius A Factor is reasonably close to the high pressure limit value, but the activation energy is significantly less than the known bond energy or energy barrier at the appropriate temperature. This serves to dramatically accelerate the reaction, instead of

slowing it down, as would occur if it were in the fall off region, and when E_a is less than ΔH_{rxn} , it also appears to violate with thermodynamics. The exception, where one would expect to have a lower E_a is only if one were well away from the high-pressure limit, implying a much lower Arrhenius A factor. The unrealistic combination of a high A and low E_a serves to dramatically, but erroneously, accelerate the reaction.

In this study we focus on thermodynamic and kinetic analysis for reaction paths of cyclopentadiene and cyclopentadienyl radical with O_2 , O and H atoms, in addition to OH and HO_2 radical. These reaction paths are radical combination or addition to unsaturated bonds in the cyclopentadienyl ring which form energized complexes that can react back to reactants or to low energy products before being collisionally stabilized. We treat all of these reactions with the bimolecular Quantum Rice Ramsperger Kassel Theory (QRRK)¹¹. We also treat dissociation of the complexes which become stabilized with unimolecular QRRK theory to account for collisional fall-off at temperatures of the experimental data we are modeling. Required thermodynamic properties for the radical intermediates were calculated using the THERM¹² computer code.

Metathesis reactions of cyclopentadiene with H, OH, HO_2 , phenyl, phenoxy, and alkyl radicals all serve to abstract the weak allylic hydrogen and form the resonantly stabilized radical. These reactions are relatively fast at combustion temperatures and serve to form and maintain a relatively high concentration of Cycpdj, which remains in thermal equilibrium with the rest of the radical pool. Clearly when the Cycpdj builds up in concentration the reverse reactions become important. The abstraction reactions, therefore, serve to shuttle the H atoms back and forth between resonantly stabilized and other species with relative concentrations controlled more by thermodynamics (equilibrium) than by kinetics. We propose that radical addition and combination reactions involving these resonantly stabilized species play a major role in the oxidation loss processes of benzene.

Addition Reactions of H, OH, and O atoms to Cyclopentadiene

The addition of a radical such as OH or H to the parent Cycpd forms an energized adduct, which can decompose to lower energy, non-cyclic products by Beta Scission (B_{sc}) reactions, dissociate back to reactants or be collisionally stabilized. There are two sites that a radical can add to the Cycpd molecule, the 1 or the 2 position, where the 5 position is carbon with 2 hydrogens. If a radical or atom adds to the 1 position, a radical is formed at the 2 position, which can B_{sc} the allylic carbon-carbon bond, opening the 5 member ring and forming a stabilized radical. If an atom or radical adds to the 2 position a radical is formed at the 1 position, which B_{sc} a vinylic carbon-carbon bond opening the ring and forming a vinylic radical. The formation of a vinylic radical is less thermodynamically favored, but the vinylic radical, if formed, will rapidly decompose, unimolecularly, by a series of scission reactions to acetylene plus a

radical.

The example of H atom adding to the double bond of CyCpd at the 1 position is shown in Figure 1. Here the cyclic radical can decompose to a lower energy linear C_5 dienyl radical, which also has a large amount of resonance stabilization and is therefore not highly reactive. The addition of H atoms to the 2 position in the ring results in a non-resonantly stabilized cyclic radical, which can either dissociate back to reactants or undergo ring opening to form a 1,4-pentadiene-1-radical (vinyllic) that will rapidly dissociate to acetylene and the relatively stable allyl radical. Thus the more energetic pathway, although slower, serves, essentially, as an irreversible sink and is important.

The addition of OH to Cyclopentadiene (Fig 2) at the 2 position forms a radical at the 3 position (carbon adjacent to the CH_2 group). This radical will either dissociate back to initial reactants or B_{sc} a carbon-carbon bond to form a vinyllic alcohol labeled C^*CCOHC^*C . (* denotes a double bond). This will either react back to the cyclic radical, beta scission to an endothermic channel forming acetylene and a resonantly stabilized primary alcohol radical of propenol as labeled in channel 3. An alternate reaction path of the linear C_5 vinyl radical, however, is a hydrogen shift from the alcohol to the vinyl group with the oxy radical then initiating the scission reaction to either vinyl + propene aldehyde or $C^*C(C^*O)C^*C + H$. These carbonyl products will eventually react to $CO +$ unsaturated C_2 and CH_3 hydrocarbons. OH adding to the 1 position will allow B_{sc} of an allylic C-C bond to form $C.C^*CC^*COH$ which is equivalent to $C^*CC^*CC.OH$, and will beta scission to $C^*CC^*CC^*O + H$. This linear unsaturated C_5H_6O will lose the carbonyl H atom (abstraction) and break down to acetylenes plus CO. Reactions of O atoms with CyCPD are also very important.

Reactions of Cyclopentadienyl Radical (CyCpdj)

CyCpdj + HO_2
In the benzene oxidation mechanism we have assembled, the reaction of CyCpdj + HO_2 is one of the most important chain branching reactions. These two radicals build up to relatively high concentrations at temperatures of the experiments we are modeling (ca 1000 - 1200 K), and this reaction is, therefore, important to reducing both radical concentrations. The potential energy level diagram illustrated in Figure 3 shows that combination of the two radicals can form a hot cyclopentadienyl hydroperoxide which will rapidly dissociate either back to reactants or to cyclopentadienyl-oxy (Cpd-oxy) radical + OH, with the products favored at these temperatures due to slightly lower exit barrier and the increased entropy. The OH product is also more reactive than HO_2 , further accelerating the overall reaction via abstraction reactions.

The Cpd-oxy radical will undergo rapid unimolecular dissociation at these temperatures via two low energy pathways shown in Figure 4. One path forms a cyclopentadienyl ketone + H atom, and the second opens the ring to a vinyllic pentadienyl aldehyde

radical. This will undergo rapid internal abstraction of the carbonylic hydrogen to form the resonantly stabilized complex shown in figure 4. The carbonyl radical formed will dissociate to CO plus a butadienyl radical which will further dissociate to acetylene + vinyl.

We note that the above Cpd-oxy radical (adduct) is also formed directly from the combination of O atoms with CyCpdj, but in this case, the adduct formed (initially) has 50 kcal/mole more energy than is needed to undergo B_{SC} reactions to the products in Fig. 4. This reaction is only limited by [O].

Several of the above reaction paths including O atom addition to either CyCpd or CyCpdj result in formation of cyclopentadien-one. This ketone can further react through addition of radical species to its unsaturated bonds, as shown in Fig. 5 for H atom addition. The initial adduct has enough energy to undergo ring opening forming a stabilized carbonyl radical, which will further decompose by unimolecular reaction to CO + butadienyl radical.

We have treated these reaction systems with the bimolecular QRRK formalism of Dean¹¹ to determine the apparent reaction rate constants to each channel including the stabilized adducts. Input parameters for the QRRK calculation are listed in below for reaction illustrated in Fig 5.

k	A	E _a (Kcal/mole)	Reference
k ₁	3.98E13	2.6	A and Ea from H + C ₂ H ₄ , ref (11)
k ₋₁	1.53E14	47.74	Thermodynamics
k ₂	7.83E14	18.22	Thermodynamics
k ₋₂	6.77E12	10.0	A TST, $\Delta S^\ddagger = -4$, Ea (Ring Strain + 5 ¹³)
k ₃	1.47E15	38.44	($\Delta H_{Rxn} + 5^{13}$)

(* denotes double bond, # denotes triple bond)

References

1. M. C. Lin and C. Y. Lin, J. Phys. Chem. 90, 425 (1986).
2. J. Manion and R. Louw, J. Phys. Chem., 93, 3563 (1989).
3. E. Ritter, J. Bozzelli and A. M. Dean, J. Phys. Chem 94, 2493. (1990), E. Ritter Ph.D Thesis NJIT (1989).
4. D. McMillen and D. Golden, Ann. Rev. Phys. Chem. 33, 493 (1982)
5. S. Stein and D. M. Golden, J Org. Chem, 42, p839 (1977)
6. E. Ritter and J. W. Bozzelli, Chemical Phys Processes in Combustion Combustion Inet., Eastern States Section Albany, NY (1989).
7. K. Brezinsky Prog in Energy Combust Science, 12, (1986).
8. C. Venkat, K. Brezinsky and I. Glassman, 19 Symp. Combustion, 143 (1982)
9. D. A. Bittker Central States Section, Combustion Institute Symposium, Indianapolis, In, May 1988.
10. L. D. Brouwer, W. M. Margraf and J. Troe, J Phys. Chem. 92, 4905 (1988).
11. A. M. Dean, J. Phys. Chem. 89, 4600, (1985).
12. THERM Thermodynamic Property Estimation of Radicals and Molecules, E. Ritter and J. W. Bozzelli, Int. J. Chem Kinetics (1991).
13. S. Stein and A Fahr, Proceedings of 22nd Comb. Inst. Symp, 1023 (1988).

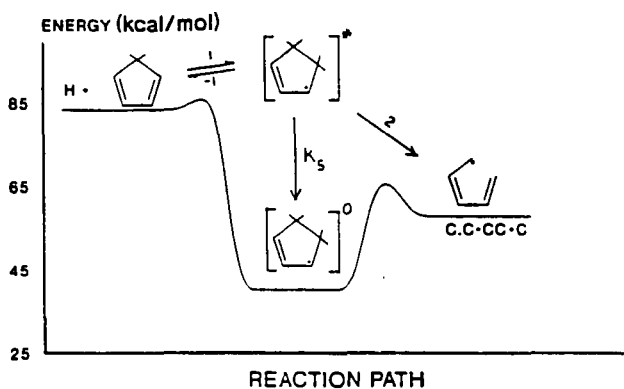


FIGURE 1. CYCLOPENTADIENE + $H \cdot \rightarrow$ PRODUCTS

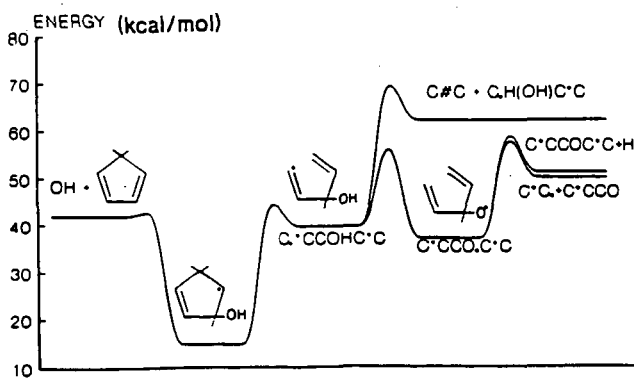


FIGURE 2. CYCLOPENTADIENE + $OH \cdot \rightarrow$ PRODUCTS

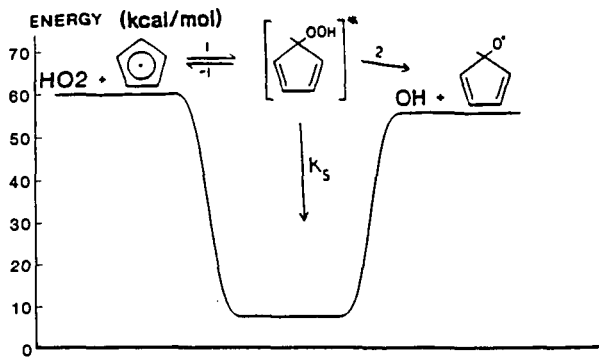


FIGURE 3. HO₂ + CYCLOPENTADIENYL RADICAL

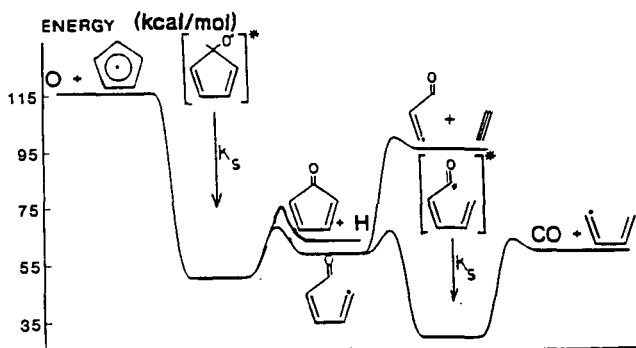


FIGURE 4. O + CYCLOPENTADIENYL RADICAL

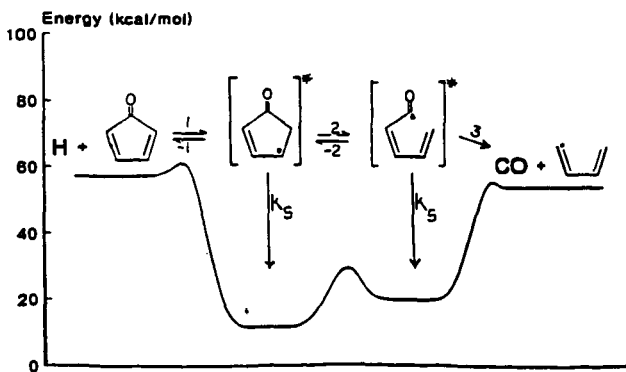


FIGURE 5. H + CYCLOPENTADIEN-ONE